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DEVELOPMENT OF A FLEXIBLE MATERIAL RESISTANT TO NITROGEN TETROXIDE AND HYDRAZINE

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DEVELOPMENT OF A FLEXIBLE MATERIAL RESISTANT TO NITROGEN TETROXIDE AND HYDRAZINE

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SCOPE

This report covers the work performed during the period of September 7, 1966 to October 7, 1966 on the "Development of a Flexible Material Resistant to Nitrogen Tetroxide and Hydrazine", Project U6046 under JPL Contract No. 951483.

The primary objectives of this program are to synthesize and evaluate selected fluorinated polymeric systems for utilization as materials of construction for the containment of nitrogen tetroxide and hydrazine type fuels. The materials and products to be studied and evaluation tests to be carried out are specified in JPL Contract No. 951483.

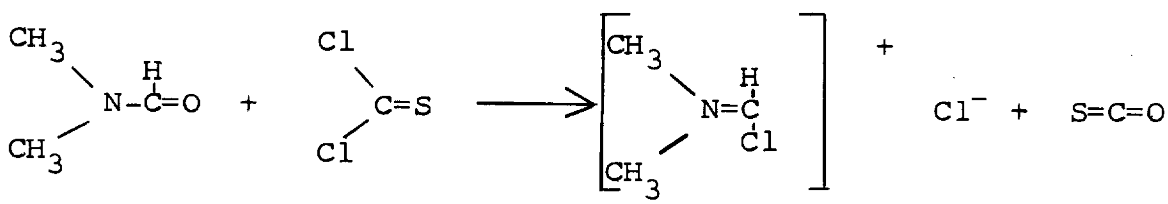
WORK PERFORMED

Preparation of Thiocarbonyl Fluoride

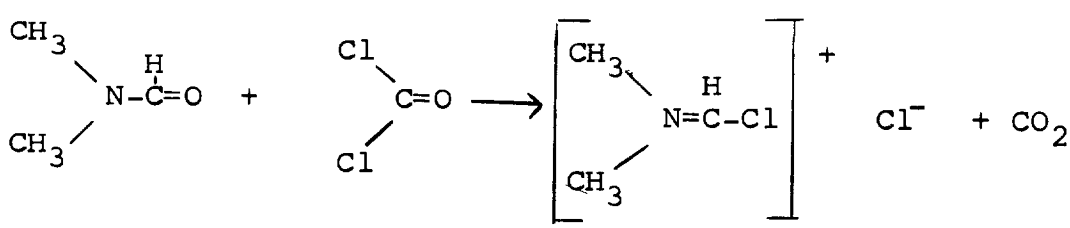
Continued difficulty has been encountered in the preparation of the thiocarbonyl chloride dimer. In order to clarify the difficulty, the reaction conditions and the isolation techniques used were re-evaluated. It was found that when the reagent was irradiated with a 300-w sun lamp at a distance of six inches for less than 24 hours and for more than 60 hours, isolation of the dimer by sublimation and by crystallization gave very poor yield. In the case of the 24-hour irradiation, this may be caused by codistillation of the dimer during evacuation of the unreacted reagent and decomposition from added heating;

irradiation for the longer time may have caused polymerization and decomposition.

It was also found that basic reagents such as pyridine and dimethylformamide, including the milder basic reagents acetone and ether, lowered the yield. These basic catalysts, used by Middleton et al (ref. 1) to dimerize perfluorothioacetone generally failed to catalyze the dimerization of thiocarbonyl chloride. For example, pyridine, reacted violently with thiocarbonyl chloride leaving a dark tarry material, and dimethylformamide formed a salt-like crystal.



Basshard and Zollinger (ref. 2) showed that phosgene and dimethylformamide react to give the following salt:



Thus, it seems that even the milder basic catalysts (acetone and ether) which were used as material transfer solvents, or as dimerizing catalysts, may have an unwanted effect. Furthermore, the inherent impurities in the thiocarbonyl chloride may have caused deleterious side reactions. Experiments were subsequently conducted to preclude the above conditions.

Experiments using irradiation times between 36 and 48 hours and eliminating the use of acetone and ether improved the yeild, although not sufficiently. In another experiment, thiocarbonyl chloride was distilled and the fraction boiling at 71-73°C was collected and irradiated for 24 hours (with 0.5 cc carbon tetrachloride). The resultant product was crystallized in the reaction flask with pentane by chilling in a dry ice-isopropanol bath; crystals were collected by filtration. The yield improved without giving any oily product. The absence of an oily material indicates some improvement over the results obtained previously. A longer reaction time (36 to 48 hours) using distilled thiocarbonylchloride is currently in progress.

Following the suggestions of Mr. David Lawson, thiocarbonyl chloride was reacted with potassium fluoride in dry tetramethylene sulfone. Two reactions were conducted: one at 75 to 80°C and the other at 100 to 110°C. The reaction product was collected in a liquid nitrogen trap with a fore ice-water trap to collect the higher-boiling product. Two mass spectrographs were made from each reaction - one from a sample taken at near liquid nitrogen temperature and the second from a sample which remained at dry ice-isopropanol temperature. The major product was found to be carbonyl sulfide. This phase will be terminated to continue other suggested alternates, such as the reaction of thiocarbonyl chloride and a molten mixed fluoride salt and the synthesis of thiocarbonyl fluoride starting with carbor disulfide and mercurous fluoride.

An attempt was made to pyrolize the dark oil formed in the dimerization reactions. From each reaction, the oil was collected and stored in benzene. Pyrolysis was performed at 250 to 300°C in a molten potassium nitrate-sodium nitrite bath. The pyrolysis experiment was unsuccessful.

Polymers from p-Hydroxybenzotrifluoride

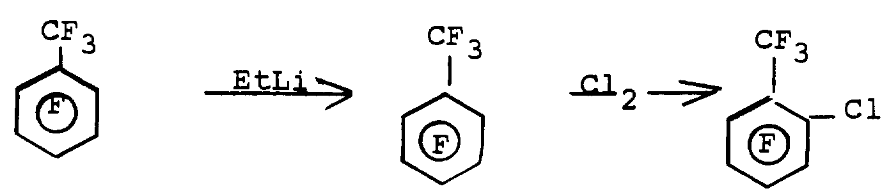
Two solution polymerizations have been carried out following the procedures of Dow Chemical Company (ref. 3). The general assumption made from their work was that the molecular weight of the polymer increases with the increase in boiling point of the solvent used. Therefore, in place of o-dichlorobenzene (b.p. 179°C), tetramethylene sulfone (b.p. 285°C, dried over molecular sieve), obtained from Phillips Petroleum Company, was substituted. The reaction mixture of p-hydroxybenzotrifluoride which was sublimed and water azeotroped with benzene, tetramethylene sulfone and 50% sodium hydride-oil dispersion was refluxed for 24 hours. The polymer obtained by precipitating in 50% methanol-H_2O was a brown colored semi-solid material.

A similar reaction was performed using potassium ter-butoxide as catalyst. The product was a tan-colored, amorphous precipitate. The physical properties and its susceptibility to nitrogen tetroxide and hydrazine will be included in the next report. These same reactions are currently being performed according to the procedures described by McMasters (ref. 4) in which the reaction proceeds from the low-temperature phenoxide stage to the high-temperature polymerization stage.

Preparation of p-Hydroxy- and o-Chloroperfluorobenzotrifluoride

Octafluorotoluene purchased from Aldrich Chemical Company was used as the starting material without further purification (a gas chromatogram showed good purity). Reacting the above compound with 1.5% sodium methoxide afforded a quantitative yield of p-methoxyperfluorobenzotrifluoride on two occasions. The purified intermediate will be cleaved with hydriodic acid or aluminum chloride as discussed by Farbes et al (ref. 5).

Simultaneously, the preparation of o-chloroperfluorobenzotrifluoride was also initiated in the following scheme of Benkeser and Severson (ref. 6).



Ethyllithium in benzene obtained from ORGMET of Hampstead, N. H., was used to obtain the lithium adduct and was directly chlorinated in the same flask. The resulting chlorinated mixture did not give a tarry material as stated in the literature. The fractionated product was submitted for analysis.

Polymers of Perfluoroglutaric Anhydride

The infrared spectra of the polyanhydride polymer which had been subjected to nitrogen tetroxide and hydrazine was determined. The samples were prepared by grinding the polymer in acetone and applying the solution on a sodium chloride window.

The polymer subjected to nitrogen tetroxide at 0°C showed evidence of degradation. Strong nitrate peaks were found at 6.1 and 7.57 microns and a weak ionic nitrate at 11.92 micron. The sample which was subjected to nitrogen tetroxide at 10°C showed no change. This is probably due to the fact that at 10°C the nitrogen tetroxide volatilized more rapidly than at 0°C, thus limiting the extent of contact with the polymer.

The polymer subjected to hydrazine could not be analyzed due to the insolubility of the product.

From the forementioned evidence and the unfavorable physical characteristics of this polymer, further investigation was terminated so that this time could be allocated to more promising areas of interest.

FUTURE WORK

Preparation of Thiocarbonyl Fluoride

A major effort will be initiated in the preparation of thiocarbonyl fluoride via the thiocarbonylchloride dimer and via the chemical syntheses suggested by Mr. David Lawson and Dr. S. F. Reed, Jr.

Polymerization of p-Hydroxybenzotrifluoride

The physical characteristics and nitrogen tetroxide- and hydrazine-susceptibility of the 24-hour reacted polymer will be elucidated.

The polymers obtained by proceeding through the low temperature phenoxide stage to the high temperature polymerization stages will be investigated.

Preparation and Polymerization of p-Hydroxy- and o-Chloroperfluorobenzotrifluoride

O-Chloroperfluorobenzotrifluoride and the partially completed synthesis of p-hydroxyperfluorobenzotrifluoride will be completed and their polymerization study initiated.

Co-Polymerization Study of Tetrafluoroethylene

Equipment and chemicals are in the process of being purchased. Reaction condition and organization of apparatus are being studied. Experiments will be carried out as soon as proper equipment is set up.

PERSONNEL

The work was performed by Mr. Terry Yamauchi and Dr. S. F. Reed, Jr. The data are recorded in Logbook C17031 and C17188.

Respectfully submitted,

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